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Analytical Description of the Pore Structure of Porous Powder Materials

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Abstract

In this chapter, we propose a method for the analytical description of the porous powder materials' (PPMs) pore distribution based on the pore structure data obtained by mercury porosimetry. The mercury porosimetry method is mostly informative and reliable when speaking about the recurrence of results as compared with other methods of pore distribution investigation. In this chapter, we present a calculation method of correcting experimental data of mercury porosimetry, based on the presentation of a porous body by a statistical model of a serial type.

Keywords: porous powder material, pore volume distribution on size, average hydraulic pore size, mercury porosimetry, statistical model of porous body

1. Introduction

Consistent with the multiple functions performed by porous powder materials (PPMs) in various technical devices, a variety of computational methods were developed to assess the effectiveness of the PPMs' varying pore structure. The relevant calculations use characteristics of the pore structure of the PPMs determined experimentally. The pore volume distribution on size and the average hydraulic pore size are considered as main, most common, characteristics of the pore structure. In this chapter, we propose a method for the analytical description of the PPMs' pore distribution based on the pore structure data obtained by mercury porosimetry. The mercury porosimetry method is mostly informative and reliable when speaking about recurrence of results as compared with other methods of pore distribution investigation. However, a pore distribution function provided by this method has a distorted character. It increases the volume of small pores that is provided by the narrowing and widening of pore

channels on the way of mercury travel. In this chapter, we present a calculation method of correcting experimental data of mercury porosimetry, based on the presentation of a porous body by a statistical model of a serial type.

2. Analytical description of the pore structure

Mercury porosimetry is the most accurate and informative method of studying the pore volume distribution on size. The essence of this method consists of measuring the quantity of mercury pressed in the pre-evacuated porous material, depending on the applied external pressure [1].

Mercury porosimeter operates as follows. The test sample is placed in a sealed cell which is evacuated; simultaneously the sample is degassed. Then, mercury is introduced into the cell so that mercury completely closes the sample. The mercury is automatically subjected to a predetermined pressure, which is left for a certain time so that the mercury fills all the pores that have the size larger than the critical value. At each table pressure value, the volume of mercury, which went down in the pores of the sample, is measured with a permittance method. According to the experimental data, the integral

$$F(d) = \frac{V(d)}{V_0} \quad (1)$$

and the differential

$$f(d) = -\frac{1}{V_0} \frac{dV(d)}{dd} \quad (2)$$

functions of pore volume distribution on size are calculated. Here $V(d)$ —the volume of mercury—went down into the sample at the pressure corresponding to the critical pore size d ; V_0 —the total amount of mercury—went down into the sample at the maximal pressure.

For processing the experimental data, the following technique was developed. Because usually the minimum and maximum pore sizes of the PPMs differ by 1–2 orders of magnitude; the logarithmically uniform pressure table is pre-assigned that corresponds to the logarithmically uniform sequence of pore size values $d_0^T, d_1^T, \dots, d_N^T$:

$$\frac{d_i^T}{d_{i-1}^T} = \text{const}, \quad i = 1, \dots, N. \quad (3)$$

However, because the automatically applied pressure is not exactly equal to the table value, and may differ from it by 1.5%, the real critical pore sizes d_i coincide with the table values with the same deviation:

$$d_i = d_i^T \pm 0.015d_i^T, \quad i = 0, \dots, N. \quad (4)$$

According to the obtained values of the volume of mercury which went down into the sample V_0, V_1, \dots, V_N , integral function of pore distribution is approximated by a finite Fourier series [2]. As a first approximation, the volume V_i is deemed as related to the values of pore size distributed logarithmically evenly between d_0 and d_N and equal to $d_0(d_N/d_0)^{i/N}$, $i = 0, \dots, N$. Assuming

$$V_{2N-i} = V_i, \quad i = 1, \dots, N, \quad (5)$$

the volume values are calculated in the points d_i by the approximating function:

$$V_i^{(j)} = \frac{a_0^{(j)}}{2} + \sum_{k=1}^{N-1} a_k^{(j)} \cos \frac{\pi k \ln \frac{d_i}{d_0}}{\ln \frac{d_N}{d_0}} + (-1)^N \frac{a_N^{(j)}}{2}, \quad i = 0, \dots, N, \quad (6)$$

where

$$a_k^{(j)} = \frac{1}{N} \sum_{m=0}^{2N-1} y_m^{(j)} \cos \frac{\pi m k}{N}, \quad k = 0, \dots, N; j = 1, \dots, J. \quad (7)$$

In the last expression in the first approximation, as it was said,

$$y_m^{(1)} = V_m, \quad m = 0, \dots, 2N-1, \quad (8)$$

and successive approximation of the volume values in the points d_i is given by the approximating function to the experimental values provided by the next iteration:

$$y_m^{(j)} = y_m^{(j-1)} + V_m - V_m^{(j-1)}, \quad m = 0, \dots, 2N-1; j = 2, \dots, J. \quad (9)$$

A satisfactory accuracy of the approximation of the experimental results (deviation less than 1%) is usually achieved when the number of iterations is $J = 5$. Obtained values of the expansion coefficients $a_k^{(j)}$ allow one to calculate the approximating function of pore volume distribution on size for any values of the pore size $d_0 \leq d \leq d_N$ by the expression:

$$F(d) = \frac{1}{V_0} \left(\frac{a_0^{(j)}}{2} \right) + \sum_{k=1}^{N-1} a_k^{(j)} \cos \frac{\pi k \ln \frac{d}{d_0}}{\ln \frac{d_N}{d_0}} + (-1)^N \frac{a_N^{(j)}}{2}. \quad (10)$$

It is easy to obtain the expression for the approximating differential function by differentiating the last expression:

$$f(d) = \frac{1}{V_0} \frac{\pi}{d \ln \frac{d_N}{d_0}} \sum_{k=1}^{N-1} k a_k^{(j)} \sin \frac{\pi k \ln \frac{d}{d_0}}{\ln \frac{d_N}{d_0}}. \quad (11)$$

Figures 1 and 2 show the processed, accordingly described, technique data on the experimental study of pore volume distribution on size of the PPMs obtained by sintering a freely poured copper powder PMS-N with a particle size from -315 to $200 \mu\text{m}$.

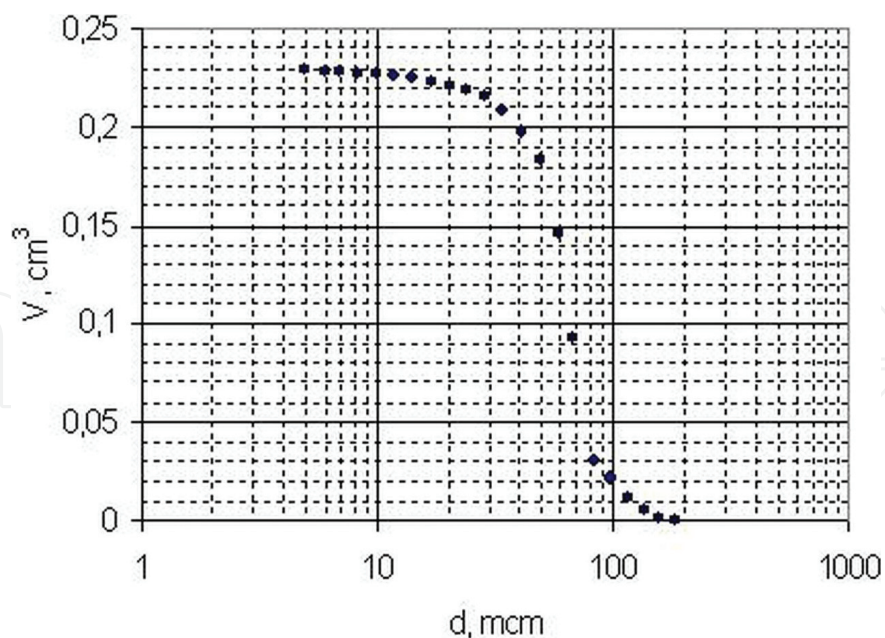


Figure 1. The results of the experimental investigation of volume pore distribution on size of sintered copper PMS-N. Particle size (–315 to +200) mm, sample weight 1.7 g.

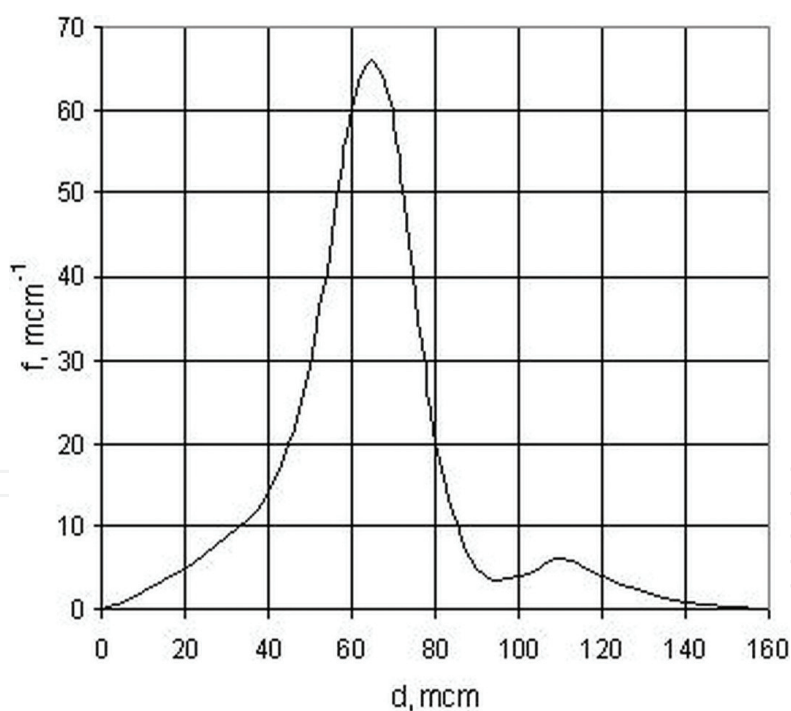


Figure 2. The approximating differential function of pore volume distribution on size of sintered copper.

The average hydraulic pore size characterizes the transport and evaporative capacity of the PPMs at full saturation of its pore space with working fluid. Experimental determination of the average hydraulic pore size is based on the use of Laplace's law. The test sample in the form of a tablet is placed in the sleeve so that the rubber gasket is tightly compressed on the side

surface of the sample (**Figure 3**). At the bottom of the sleeve is a socket, connected to a hose of sufficient length, filled with a liquid which completely wets the sample. The lower end of the hose is placed in a vessel containing the same liquid. A slow rise of the sample is produced. At the moment of separation of the liquid in the hose from the sample, the height of the sample over the liquid level in the vessel h is recorded. The average hydraulic pore size d is calculated by the expression:

$$d = \frac{4\sigma}{\rho g h'} \quad (12)$$

where σ is the surface tension, ρ is the density of the liquid, and g is the acceleration of free fall.

In case of partial draining of the pore space (e.g., with intense evaporation of the liquid inside the PPMs, the action of the mass forces, etc.), the pore size distribution becomes significant. The question arises about the relationship between the function of pore distribution and average pore size of PPMs. Special experiments and subsequent calculations showed that for the PPMs, fabricated with the same technology from different fractions of one powder, such a relationship exists. If the integral function of pore distribution of PPMs with the average

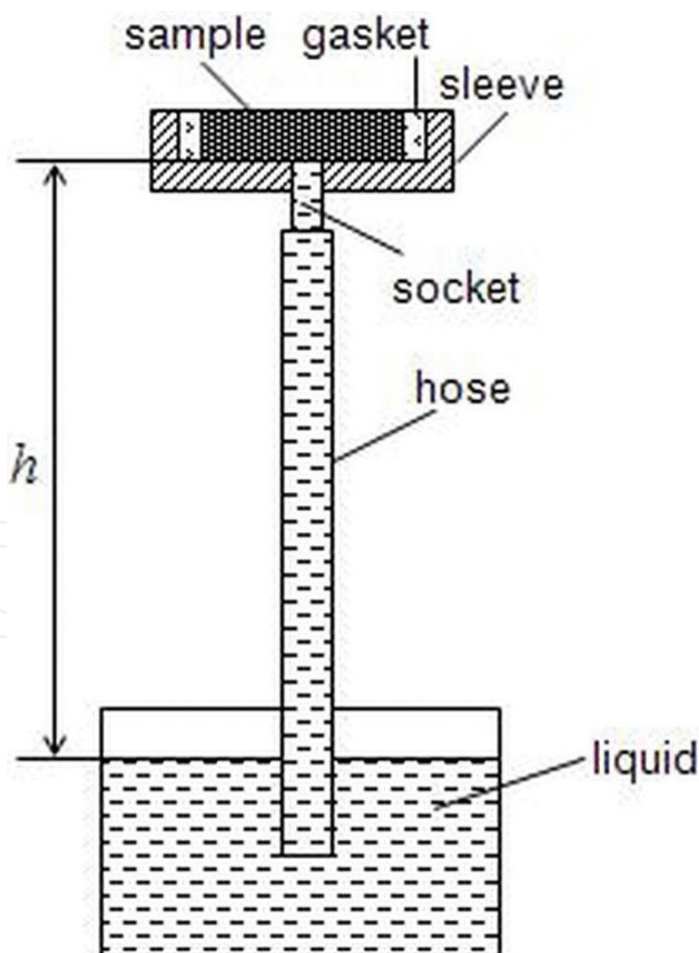


Figure 3. Experimental determination of the average hydraulic pore size.

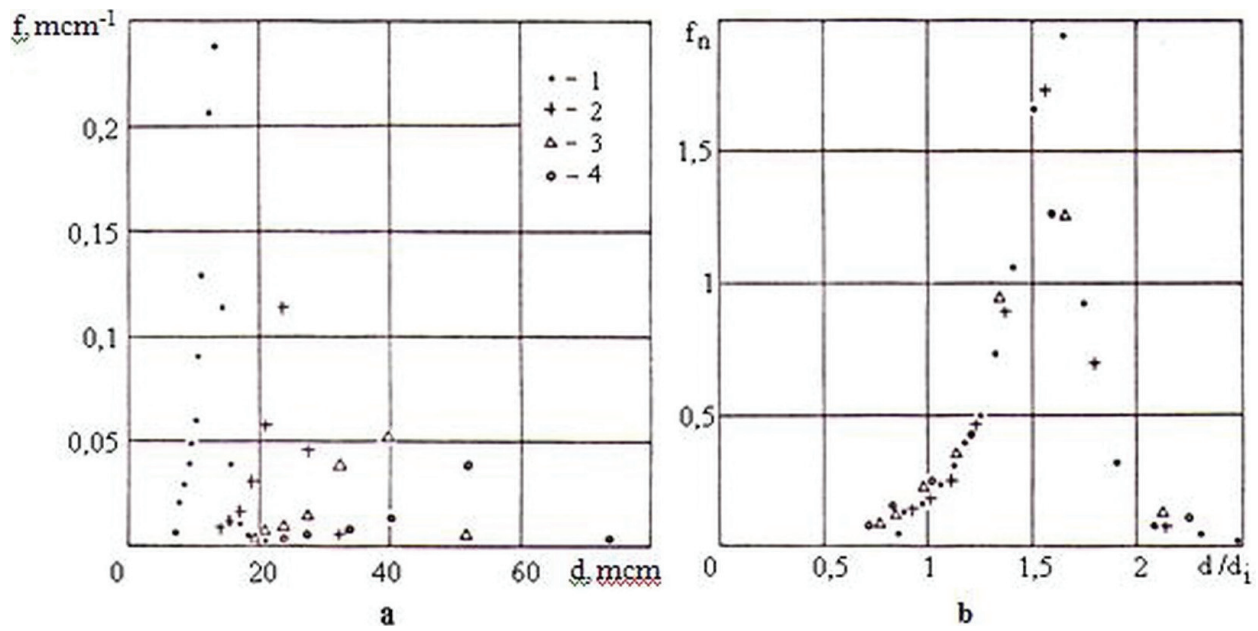


Figure 4. Experimental data on pore distribution of the porous bronze in conventional coordinates (a) and the normalized coordinates (b): 1, particle size $<63 \mu\text{m}$, $d_1 = 8.1 \mu\text{m}$; 2, $63\text{--}100 \mu\text{m}$, $d_2 = 15.2 \mu\text{m}$; 3, $160\text{--}100 \mu\text{m}$, $d_3 = 24.2 \mu\text{m}$; 4, $200\text{--}160 \mu\text{m}$, $d_4 = 33 \mu\text{m}$.

hydraulic pore size of d_1 is $F_1(d)$, then the integral function of pore distribution of PPMs with the average hydraulic pore size of d_2 can be calculated from the function $F_1(d)$ by the coordinate transformation $d \rightarrow d' = d d_1/d_2$:

$$F_2(d) = F_1\left(d \frac{d_1}{d_2}\right); \quad (13)$$

respectively, for the differential pore distribution function:

$$f_2(d) = -\frac{dF_2(d)}{dd} = -\frac{dF_1(d')}{dd'} \frac{dd'}{dd} = f_1\left(d \frac{d_1}{d_2}\right) \frac{d_1}{d_2}. \quad (14)$$

Express provision is illustrated in **Figure 4**, where the experimental data for a porous bronze material BrOF10-1 depicts in the conventional coordinates (f, d) (a) and in the coordinates normalized by the average hydraulic pore size ($f_n, \frac{d}{d_i}$) (b). As shown, in the normalized coordinates the experimental points lie almost on the same curve.

3. Method to correct the data of mercury porosimetry

It is known [1] that pore distribution function, derived from the method of mercury porosimetry, is of a distorted character. It raises the volume of small pores that is caused by narrowing and widening porous channels on the way of mercury travel. Therefore, to use the data of mercury porosimetry in calculations of operational properties of porous materials, a correction of this data is necessary.

The developed method of correction of mercury porosimetry data is based on using a statistical model of a porous body of a serial type [3, 4]. In this model, a porous body is presented as a block of parallel capillaries, each of which consists of a number of successively disposed cylindrical elements. The diameter ζ and the length ξ of each element are random values, which do not depend on adjacent elements and are distributed with the probability density $\Psi(\zeta, \xi)$. Such a model is very similar to a real PPM structure and discloses the corrugateness of channels, as well as the accidental character of narrowing and widening.

Let us consider a process of mercury pressing into a model porous body. Let the mercury be on the left from the plane $x = 0$; on the right there is a porous body as a layer with the thickness l_0 . If mercury pressure is p , it penetrates in the elements with the diameter, exceeding the critical one $\zeta_p = 4\gamma \cos\Theta/p$, where γ is a coefficient of the mercury surface tension and Θ is an angle of moistening with the mercury of the porous body material. Thereby, mercury will enter the ν first

$$z_\nu = \sum_{i=1}^{\nu} \xi_i. \quad (15)$$

elements, if $\zeta_1, \dots, \zeta_\nu > \zeta_p$, and $\zeta_{\nu+1} < \zeta_p$. Then the length of the mercury part of the given capillary is

Let the function of the mercury capillary part length be $P(z)$. If suppressing in k -element, a corresponding distribution function is $P_k(z)$, and a probability density is $\Psi_k(z)$:

$$P_k(z) = \int_0^z \Psi_k(x) dx, \quad (16)$$

then

$$P(z) = \sum_{k=1}^{\infty} \omega_k P_k(z), \quad (17)$$

where ω_k is the probability of mercury suppression in the k -element, distributed as per a geometrical law:

$$\omega_k = \mu^{k-1} (1 - \mu), \quad (18)$$

μ is the relative number of elements with the diameter exceeding a critical one.

$$\mu = \int_{\zeta_p}^{\infty} d\zeta \int_0^{\infty} \Psi(\zeta, \xi) d\xi. \quad (19)$$

Under pressure p all the ξ_i are distributed in the same way with the probability density:

$$\Phi_p(\xi) = \int_{d_p}^{\infty} \Psi(\zeta, \xi) d\zeta / \int_0^{\infty} d\xi \int_{d_p}^{\infty} \Psi(\zeta, \xi) d\zeta. \quad (20)$$

$\Psi_k(x)$ is calculated via $\Psi_{k-1}(x)$ as follows:

$$\Psi_k(x) = \int_0^x \Psi_{k-1}(x') \Phi_p(x - x') dx'. \quad (21)$$

Substituting Eq. (21) in Eq. (16), we shall get:

$$P_k(z) = \int_0^z \Phi_p(x) P_{k-1}(z - x) dx. \quad (22)$$

Next, substituting Eq. (22) in Eq. (17):

$$P(z) = (1 - \mu)P_1(z) + \sum_{k=2}^{\infty} \mu^{k-1} (1 - \mu) \int_0^z \Phi_p(x) P_{k-1}(z - x) dx = \int_0^z \Phi_p(x) (1 - \mu + \mu P(z - x)) dx. \quad (23)$$

Thereby, we derived an equation to find a function of the length z distribution of the mercury capillary part under the pressure in the mercury p , which is an integral Volterra equation of the second gender:

$$P(z) = \int_0^z \Phi_p(x) (1 - \mu + \mu P(z - x)) dx. \quad (24)$$

Thereafter we shall consider a model, in which all the elements have the same length ξ_0 , that is, the density of the distribution probability ξ_i is equal to the δ -function under any pressure p :

$$\Phi_p(\xi) = \delta(\xi - \xi_0). \quad (25)$$

Justifying such a simplification is based on a smooth-changing a pore diameter. When the value of ξ_0 is rather small, a transversal size of the pore part, the length of which is ξ_0 , may be considered as constant. Substituting Eq. (25) in (24), we derive an equation for $P(z)$:

$$p(z) = 1 - \mu + \mu p(z - \xi_0), \quad (26)$$

giving a step-by-step solution:

when	$z < 0$	$P(z) = 0;$
when	$0 \leq z < \xi_0$	$P(z) = 1 - \mu;$
.....		
when	$(n-1)\xi_0 \leq z < n\xi_0$	$P(z) = 1 - \mu^n,$

(27)

where $n = l_0/\xi_0$ is the number of elements in one capillary.

The derived solution for $P(z)$ must be connected with an experimental value of the entered mercury volume. If in the given capillary the length of the mercury part is z , the mercury volume in it is

$$v_{1p}(z) = v_1 z \int_{d_p}^{\infty} f(\zeta) d\zeta, \quad (28)$$

where $f(\zeta)$ is the true density of pore volume distribution on sizes and v_1 is a medium volume of capillary length unit. A total volume of mercury, entered under the pressure p , is

$$v(p) = \int_0^{l_0} N_0 \frac{dP}{dz} v_{1p}(z) dz + v_1 l_0 \int_{l_0}^{\infty} N_0 \frac{dP}{dz} dz \int_{\zeta_p}^{\infty} f(\zeta) d\zeta, \quad (29)$$

where N_0 represents a total quantity of the capillaries. In the expression (29), the first component considers the volume of partially filled capillaries, and the second component considers the volume of fully filled ones. Convert the expression (29), considering $V_0 = v_1 N_0 l_0$ (V_0 is the total volume of the porous area):

$$v(p) = V_0 \left(1 - \frac{1}{l_0} \int_0^{l_0} P(z) dz \right) \int_{d_p}^{\infty} f(\zeta) d\zeta. \quad (30)$$

Using the solution (27), we may make a calculation:

$$\frac{1}{l_0} \int_0^{l_0} P(z) dz = 1 - \frac{\mu}{n} \frac{1 - \mu^n}{1 - \mu}. \quad (31)$$

Substituting Eq. (31) into Eq. (30):

$$v(p) = V_0 \frac{\mu}{n} \frac{1 - \mu^n}{1 - \mu} \int_{d_p}^{\infty} f(\zeta) d\zeta. \quad (32)$$

A dependence exists between the functions $\mu(\zeta)$ and $f(\zeta)$:

$$\frac{d\mu}{d\zeta} = \frac{f(\zeta)}{s\zeta^2}, \quad (33)$$

where we use the designation, $s = \int_0^{\infty} \frac{f(\zeta)}{\zeta^2} d\zeta$.

Using Eq. (33), let us convert an integral in Eq. (32) (later on for convenience of writing let us consider $v = v(d)$):

$$\int_{\zeta}^{\infty} f(\zeta) d\zeta = -s \int_{\zeta}^{\infty} \frac{d\mu}{d\zeta} \zeta^2 d\zeta = s \left(\mu \zeta^2 + 2 \int_{\zeta}^{\infty} \mu \zeta d\zeta \right), \quad (34)$$

Substituting Eq. (34) in Eq. (32), we get:

$$\frac{bv}{\mu} \frac{1-\mu}{1-\mu^n} - \mu \zeta^2 = 2 \int_{\zeta}^{\infty} \mu \zeta d\zeta, \quad (35)$$

where there is marked $b=n/(sV_0)$. Differentiating the expression (35) on d , we get the following equation after converting:

$$\frac{d\mu}{d\zeta} = \frac{b \frac{dv}{d\zeta} \mu (1-\mu) (1-\mu^n)}{\mu^2 \zeta^2 (1-\mu^n)^2 - bv((1-\mu)n\mu^n - 1 + \mu^n)}, \quad (36)$$

which forms the Cauchy problem together with a boundary condition

$$\mu(\zeta_{\min}) = 1 \quad (37)$$

to determine a true function of pore quantity distribution on sizes $\mu(\zeta)$. In Eq. (21), the values b and n are indefinite and are connected with the desired function $\mu(\zeta)$. Therefore, to solve the Cauchy problem there is an iterative method as follows.

Zero approximation $\mu_0(\zeta)$ is obtained, considering:

$$f_0(\zeta) = -\frac{1}{V_0} \frac{dv}{d\zeta}; \quad s_0 = \int_0^{\infty} \frac{f_0(\zeta)}{\zeta^2} d\zeta; \quad \xi_{00} = \int_0^{\infty} \zeta f_0(\zeta) d\zeta; \quad n_0 = \frac{l_0}{\xi_{00}}; \quad b_0 = \frac{n_0}{s_0 V_0}, \quad (38)$$

where l_0 is the size of the porous material sample being investigated in the direction of mercury travel. The following approximations $\mu_i(\zeta)$ are obtained using the following calculations:

$$f_i(\zeta) = \frac{\frac{d\mu_{i-1}}{d\zeta}}{2 \int_0^{\infty} \mu_{i-1} \zeta d\zeta}; \quad s_i = \sqrt{\frac{s_{i-1} \frac{1}{\int_0^{\infty} \mu_{i-1} \zeta d\zeta}}{2 \int_0^{\infty} \mu_{i-1} \zeta d\zeta}}; \quad \xi_{0i} = \frac{3 \int_0^{\infty} \mu_i \zeta^2 d\zeta}{2 \int_0^{\infty} \mu_{i-1} \zeta d\zeta}; \quad n_i = \frac{l_0}{\xi_{0i}}; \quad b_i = \frac{n_i}{s_i V_0}. \quad (39)$$

Calculation of $\mu_i(\zeta)$ on each step of the iteration is made by the Runge-Kutta method [5]; therewith, the initial value of the calculated function is $\mu(\zeta_{\min}) = 1$, and the derivative is calculated using the equality

$$\lim_{\mu \rightarrow 1} \frac{1-\mu}{1-\mu^n} = \frac{1}{n}, \quad (40)$$

with which it is possible to obtain:

$$\lim_{\mu \rightarrow 1} \frac{d\mu}{d\zeta} = \frac{b \frac{dv}{d\zeta}}{n\zeta^2 - \frac{n-1}{2}bv}. \quad (41)$$

In **Figure 5** the results of calculating the functions of pore volume on size distribution from Eq. (36) and—for comparison—directly from the experimental data are given. It is seen that as a result of data correction of mercury porosimetry, the curves of pore distribution displace considerably in the direction of large pores.

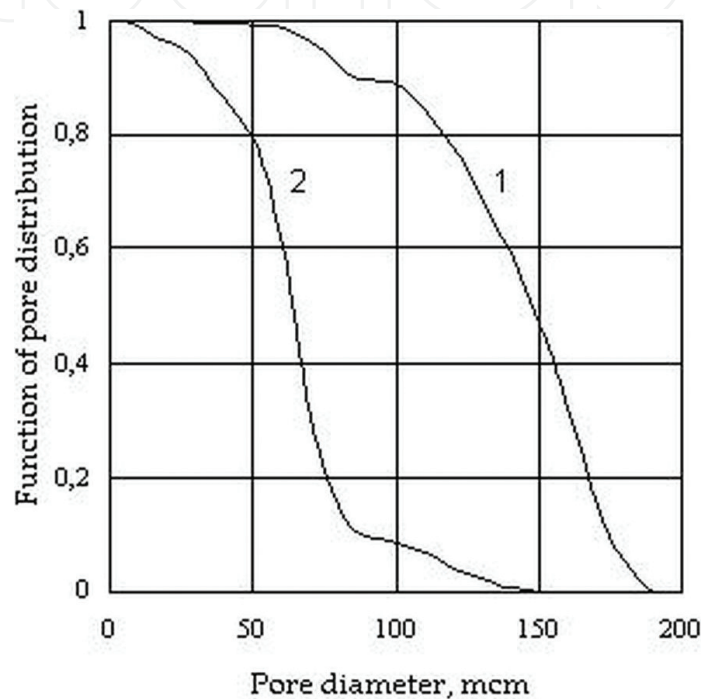


Figure 5. Function of pore volume distribution on sizes, calculated by the developed methodic (1) and directly from experimental data (2).

4. Conclusions

The relationship between the function of pore distribution and average hydraulic pore size, eliminating the need for a time-consuming set of experiments to determine the function of pore distribution of porous powder material, allowing to calculate the pore distribution function of porous powder material with any hydraulic average pore size from the known pore distribution function of the reference porous powder material with the fixed average hydraulic pore size, is explained.

The true function of pore distribution, obtained as a result of correcting mercury porosimetry data, enables to improve considerably the accuracy of calculations of processes and facilities parameters, where porous powder materials are used.

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